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Modified cassava starches as corrosion inhibitors of carbon steel: An electrochemical and morphological approach

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ABSTRACT

The physical and chemical modification of cassava starch was carried out to prepare compounds that were evaluated as corrosion inhibitors of carbon steel under alkaline conditions in 200 mg L^{-1} NaCl solutions. Two species were tested: an activated starch (AS) and a carboxymethylated starch (CMS) with two different degrees of substitution (*DS*). The success of the chemical procedure was confirmed by ^{13}C NMR. The *DS* was determined by back titration and products with 0.13 ($CMS_{0.13}$) and 0.24 ($CMS_{0.24}$) were obtained. The inhibitive properties were studied by means of electrochemical impedance spectroscopy. It was found that modified starches have corrosion inhibitive properties and that their protection level depends on the type and amount of active groups present in the molecules. AS showed better performance than CMS, whose inhibition ability increases with the degree of substitution. This result was explained by the strong ionic interaction between AS and ferrous cations, which was confirmed by the electrostatic potential mapping of the monomeric units. After the corrosion experiments, the surfaces also were investigated through atomic force microscopy. It was found that a densification of the inhibitive layer was responsible for the higher protection level afforded by AS after 24 h of immersion.

1. Introduction

Corrosion problems are the main degradation cause of cooling water systems made of carbon steel. This phenomenon entails economic costs due to, for example, metallic material loses and bacteria development. In order to prevent degradation of these systems, water is frequently treated with formulations composed of corrosion inhibitors and biocides (Frenier, 2000).

Studies on inhibitors have evolved since 1950; at the beginning, the investigations were focused on the efficiency evaluation of chromates, nitrates, and borates, which showed high efficiency, but also high toxicity for the human being (Kàlmàn, 1990). Other compounds, economically profitable, such as metallic cations, polyphosphates, gluconates, vanadates, molybdates, phosphonates, polyacrylates, and carboxylates have also been evaluated (Frenier, 2000). However, these compounds have been banned in environmental regulations because they exhibit low biodegradability and are responsible for the eutrophication phenomenon (Fiaud, Pébère, & Zucchi, 2002). From the late 80s, most corrosion inhibitors studies have been focused on the development of "environmental friendly" compounds in response to legislation changes concerning environmental protection. This term includes formulations that are not toxic to humans, have low environmental impact, optimal biodegradability, and maintain their efficiency and cost-effectiveness. Thus, since the 90s, many investigations have been related to the evaluation of natural compounds as corrosion inhibitors; in this sense, some amino acids, vitamins, plant extracts, and soluble natural polymers have been tested (Abd El Haleem, Abd El Rehim, & Shalaby, 1986; Bouyanzer, 2004; Bouyanzer, Hammouti, & Majidi, 2006; Chauhan & Gunasekaran, 2007; El-Etre, 2006; El-Etre, 2007; El-Etre, 2008; Gunasekaran & Chauhan, 2004; Ismail, 2007; Oguzie, 2001; Radojcic, Berkovic, Kovac, & Vorkapic-Furac, 2008; Rahim et al., 2007; Sugama & DuVall, 1996). Nevertheless, few investigations report the behavior of these compounds in neutral/alkaline environments (Abd El Haleem et al., 1986; Bouyanzer, 2004; Bouyanzer et al., 2006; Chauhan & Gunasekaran, 2007; El-Etre, 2006; El-Etre, 2007; El-Etre,

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2008; Frenier, 2000; Ismail, 2007; Oguzie, 2001; Rahim et al., 2007; Sugama & DuVall, 1996) in comparison with those carried out in acid medium. It is therefore the aim of this study is to evaluate cassava starches as corrosion inhibitors of carbon steel in alkaline sodium chloride solution.

Starch is a natural polymer, highly available at low cost, renewable, and biodegradable. It is widely used in different industries such as pharmaceutical, papermaking, textile, and in food preparation. However, native starch presents some drawbacks such as low water solubility and poor stability when it is used at low pH (Burrell, 2003). Physical and/or chemical modifications are therefore interesting alternatives to develop new products, preserving petrochemical resources and improving specific starch properties (Balsamo et al., 2010; Heinze & Koschella, 2005; Rivero, Balsamo, & Müller, 2009; Singh, Kaur, & McCarthy, 2007). In this work two types of modified cassava starches were prepared in order to be studied as corrosion inhibitors: AS, a cassava starch that was modified through gelatinization and activation and CMS (carboxymethylated starch) with two different degrees of substitution (*DS*). These species were tested as corrosion inhibitors of carbon steel in an alkaline 200 mg L^{-1} NaCl solution that is a simplification of the chemical composition of tap water.

It is important to point out that, up to our knowledge, few works have been reported in the literature in which starch has been used to protect metals against corrosion. Sugama and DuVall (1996) reported the use of potato starch coatings for aluminum. They found that these coating films displayed a low susceptibility to moisture and improved impedance (in $\Omega\,cm^2$) by two orders of magnitude over that of the substrate. Abd El Haleem et al. (1986) have evaluated a starch among several natural compounds to provide protection to pitting corrosion of steel; nevertheless, they did not specify the kind of starch they employed. More recently, Rosliza and Wan Nik reported in 2009 the use of cassava starch to improve the corrosion resistance of an aluminum alloy in seawater. They found that the introduction of native tapioca starch minimized the weight loss and abridged aluminum dissolution in seawater.

2. Experimental

2.1. Preparation of modified cassava starches

Corrosion inhibitors, AS and CMS, were prepared from native cassava starch (30% amylose), supplied by Agroindustriales Mandioca S.A., Venezuela, following the procedure described by Feijoo et al. 50 g of native starch was placed in a glass reactor with distilled water (10%, w/w) and 250 ml of a 10% (w/v) NaOH aqueous solution was added. The slurry was heated up to 60 °C and kept at that temperature under mechanical agitation for 2 h in order to activate the starch molecules. A fraction of this mixture was precipitated and washed by adding ethanol in order to obtain the activated starch (AS). Then, the temperature of the remaining fraction was reduced down to 50 °C and an aqueous solution (10%, w/v) of monochloroacetic acid (MCAA) was added in order to synthesize the carboxymethylated starch (CMS); for this chemical modification a molar ratio NaOH:AGU:MCAA of 2:1:1 was used, where AGU refers to the starch anhydroglucose unit. The carboxymethylation process was carried out for 3 h under mechanical agitation. The final product, CMS, was precipitated and washed by adding ethanol. Both products, AS and CMS, called from now on “inhibitors”, were lyophilized for 48 h, and stored under vacuum at 4 °C.

2.2. Characterization of the inhibitors

The inhibitors were characterized using Nuclear Magnetic Resonance. ^{13}C NMR spectra of AS and CMS were collected on a Bruker AVANCE-500, 125.75 MHz, at 70 °C, using DMSO-d_6 and D_2O, respectively. For this purpose, the samples were previously dissolved at room temperature and kept under agitation for 24 h.

The degree of substitution of CMS, *DS*, defined as the average of hydroxyl groups substituted per AGU unit, was determined by an acid–base back titration (Contó, 2008; Heinze, Pfeiffer, Liebert, & Heinze, 1999; Stojanovi, Jeremi, Jovanovi, & Lechner, 2005). For this purpose, the CMS was dispersed in acetone under magnetic stirring and transformed into its protonated form (H-CMS) by adding a 6 M HCl aqueous solution and stirring for 30 min. The precipitate was re-dispersed in acetone, filtered, and lyophilized for 24 h. Then, 25 ml of a 0.04 M NaOH solution and 75 ml of distilled water were added to 0.1250 g (±0.0001) of CMS and agitated during 4 h before titration. The excess of alkali was back titrated with a standard 0.05 M HCl solution using phenolphthalein as indicator. A native starch sample was titrated as a blank reference. The *DS* was determined using the following equation:

$$DS = \frac{MW_{\mathrm{AGU}}(V_{\mathrm{blank}} - V_{\mathrm{sample}})N}{W - 58(V_{\mathrm{blank}} - V_{\mathrm{sample}})N} \qquad (1)$$

where MW_{AGU} is the molar weight of the anhydroglucose unit (162 g/mol), V_{blank} and V_{sample} are the HCl volumes used for titration of the blank and sample, respectively, W is the weight of the sample (g), and N is the normality of the HCl solution.

2.3. Theoretical details

Electrostatic potential [$V(r)$] mapping of the repetitive unit of AS and CMS was studied in order to explore the nature of active sites. These calculations are based on the model proposed by Politzer and Sjoberg, who have shown that by computing $V(r)$ on the 0.002-electron/bohr^3 contour isosurface (Sjoberg & Politzer, 1990) of the molecular electronic density $\rho(r)$, it could quantify the susceptibility of molecules to electrophilic and/or nucleophilic attack. In other words, this methodology allows determining Lewis acid and basic sites in a molecule (Aray et al., 2003; Aray, Rodríguez, Coll, González, & Márquez, 2004; Gadre & Shirsat, 2000; Leboeuf, Koster, Jug, & Salahub, 1999; Murray & Sen, 1996; Orozco & Luque, 1996; Politzer & Truhlar, 1982), which correspond to electron-poor and electron-rich zones of the repetitive unit, respectively. Additionally, the active sites' susceptibility can be quantified determining the minimum and maximum $V(r)$ values at the determined host zones using a Newton–Raphson technique similar to those that have been previously reported by Aray et al. for the study of the electronic density and electrostatic potential topology (Aray et al., 2003; Aray et al., 2004; Aray, Rodríguez, Coll, Rodríguez-Arias, & Vega, 2005). DMol^3 program (Delley, 1990; Delley, 2000) was used to calculate the molecular electronic density ($\rho(r)$) and $V(r)$. DMol^3 calculates variational self-consistent solutions to the density functional theory (DFT) equations, expressed in an accurate numerical atomic orbital basis. The solutions to these equations provide the molecular electron densities, which can be used to evaluate the total electrostatic potential of the system. The correlation and exchange effects were considered using the gradient generalized approximation (GGA) and the functional Perdew-Wang 91 (Perdew & Wang, 1992). The numerical double-zeta plus polarization basis set (DNP) was used in all calculations.

2.4. Corrosion experiments

The inhibitive properties of modified cassava starches were evaluated using electrochemical impedance spectroscopy (EIS). This technique was coupled with a rotating disk electrode with a fixed rotation speed of 1000 rpm. Impedance diagrams were performed using a Gamry Potentiostat DC-105 model. Electrochemical impedance measurements were obtained at the corrosion potential. They were carried out under potentiostatic regulation in a frequency range of 100 kHz to 6 mHz with eight points per decade using a 10 mV peak-to-peak sinusoidal potential.

The corrosive medium was a 200 mg L^{-1} sodium chloride solution in contact with air, maintained at 25 °C. This medium represents a simplified sample of the chemical composition of natural waters, often employed by other authors (Duprat, Lafont, Dabosi, & Moran, 1985; Ochoa, Moran, & Pébère, 2004; Ochoa, Moran, Pébère, & Tribollet, 2005). The inhibitive solutions were prepared by adding 600 mg of modified starches, AS or CMS, to 150 mL of the corrosive solution and heating at 30 °C under magnetic stirring during 5 min. Then, this solution was transferred to a larger flask to complete 1 Liter with the remaining corrosive solution. Finally, this 600 mg L^{-1} solution was allowed to cool down to room temperature under agitation. The pH of the solutions was modified by adding NaOH in order to study the inhibitive properties of the starch solutions at pH=10.

Corrosion experiments were performed in a standard Pyrex® double wall cell with platinum grid and a saturated calomel electrode (SCE) as a counter-electrode and reference, respectively. The working electrode was a rod of XC 35 carbon steel having a cross-sectional area of 0.79 cm^2, whose nominal chemical composition is 0.35C, 0.65Mn, 0.25Si, 0.035P, 0.035S, and Fe balance. The electrode surface was covered by a heat-shrinkable sheath to leave only the cross-sectional area of the carbon steel cylinder in contact with the corrosive solution. Before electrochemical tests, steel samples were polished with SiC paper down to grade 1200. They also were cleaned with ethanol, rinsed with distilled water, and dried with warm air.

2.5. Surface analysis

Once the corrosion tests were carried out, photographs of the electrodes surfaces were taken with a stereoscopic magnifier. The inhibitive layer formed in the presence of the starch molecules was also analyzed by means of atomic force microscopy (AFM) with an Agilent 5500 Scanning Probe Microscope. AFM images were obtained using Acoustic AC Mode (AAC Mode) with a cantilever oscillation frequency of 155 kHz. For this purpose, carbon steel samples were immersed during 6 and 24 h in the solution containing the inhibitor. Images were taken at the center and periphery of the surface and processed with Picoscan Image 5 software obtaining topography, amplitude, and phase images.

3. Results and discussion

3.1. Structural characterization of modified starches

In a previous work, Feijoo et al. investigated different parameters in order to optimize the reaction conditions for producing carboxymethylated starch (CMS). Based on their work, we selected the conditions indicated in the experimental part to obtain a good balance between the degree of substitution (*DS*) and the molecular weight. It must be remarked that under these reaction conditions starch destructurization or gelatinization takes place. The chemical changes of the starch were verified by ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of activated starch is shown in Fig. 1. It exhibits the characteristic peaks of the anhydroglucose unit (Atichokudomchai & Varavinit, 2004; Chi & Txu, 2008; Wang, Yu, & Yu, 2008) at 78.78, 73.30, 71.98, and 71.64 ppm, which correspond to C4, C5, C3, and C2. Other two signals are observed at 100.85 and 100.27 due to C1 (1–6) and C1 (1–4), i.e., to C1 in amylose and amylopectine, respectively, while the signals of C6 (1–6) and C6 (1–4) appear at 60.89 and 60.54 ppm. In Fig. 2a, it is shown the ^{13}C NMR spectrum for one of the CMS samples; the introduction of the carboxymethyl moieties results in a new peak at ~70.6 ppm due to the C7 methylene group (Lazik, Heinze, & Pfeiffer, 2002). Nevertheless, it should be mentioned that this signal might be overlapped by the terminal C4 groups of starch. For this reason, we

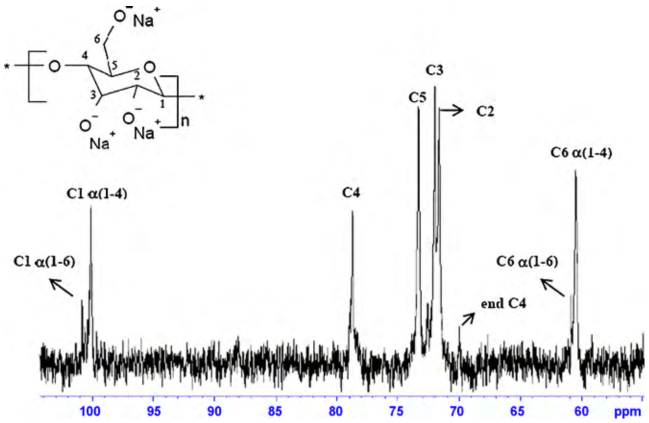

Fig. 1. ^{13}C NMR spectrum of AS in DMSO-d_6 at 70 °C.

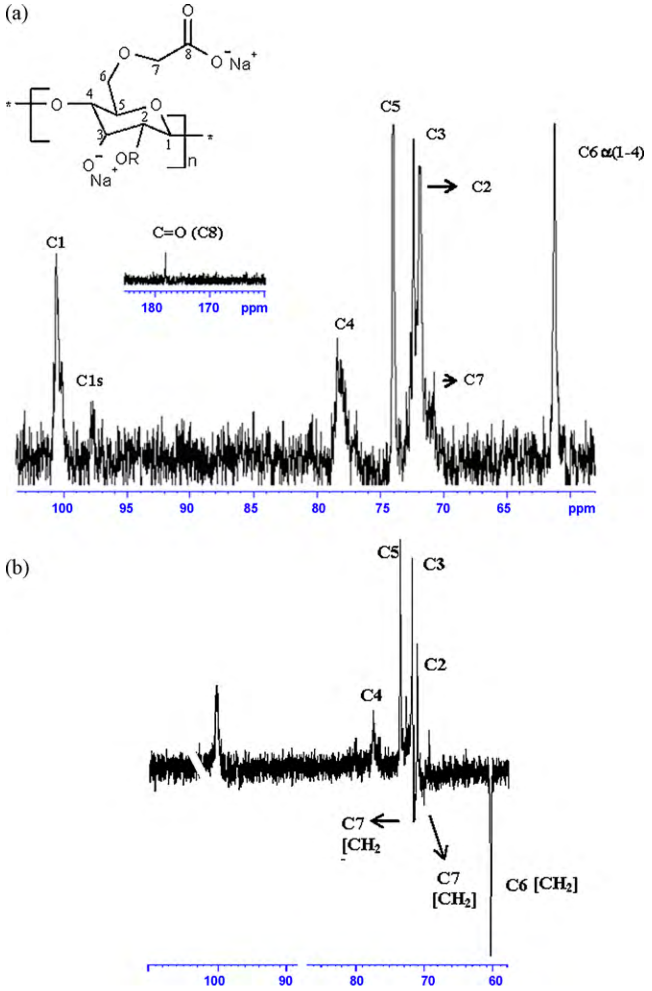

Fig. 2. (a) ^{13}C NMR and (b) DEPT 135 spectra of $CMS_{0.24}$ in D_2O at 70 °C. R = Na^+ or $CH_2COO^-Na^+$.

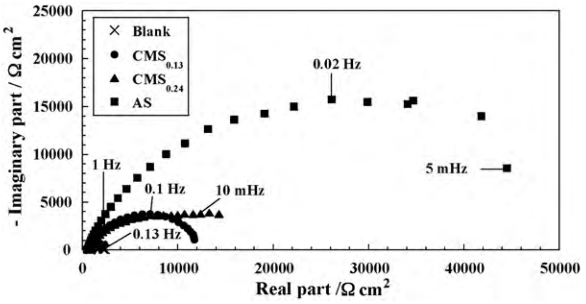

Fig. 3. Electrochemical impedance diagrams obtained after 2 h of immersion at E_{corr} in the 200 mg L^{-1} NaCl solution and in the presence of 600 mg L^{-1} of each inhibitor.

performed DEPT 135 experiments (Fig. 2b); the negative peaks of the methylene groups C7 may now be unambiguously identified at 70.30 and 71.70 ppm when the substitution has taken place on O-6 and O-2. The carboxymethylation on O-2 (C-1s) may also be identified in Fig. 2 by the appearance of a signal at ∼97.6 ppm. In addition, the peak at 178 ppm, which corresponds to the carbonyl C8 group, evidences the modification on O-6. The transformation of the carboxylate groups into carboxylic groups allowed us the estimation of a degree of substitution (*DS*), which was of 0.13 ± 0.03 (CMS$_{0.13}$) and 0.24 ± 0.04 (CMS$_{0.24}$) for the two samples that were prepared.

3.2. Evaluation of the corrosion inhibitive properties

Fig. 3 shows the electrochemical impedance diagrams recorded at the corrosion potential after 2 h of immersion in solutions containing 600 mg L^{-1} of AS, CMS$_{0.13}$, and CMS$_{0.24}$. They are compared with the diagram obtained for the blank solution. The corrosion potential and the polarization resistance values (R_p) obtained from these diagrams are listed in Table 1. R_p values were obtained by extrapolating the impedance spectra on the real axis at the lower frequency domain and these values are inversely proportional to the electrode corrosion rate. It may be observed that the diagrams exhibit one capacitive loop whose size increases in the presence of inhibitors. This is in agreement with the significant increase of the R_p values presented in Table 1 when starch molecules are added to the corrosive solution. In addition, it should be remarked that in the presence of these species, the polarization resistance values increase in the following order CMS$_{0.13}$ < CMS$_{0.24}$ < AS. This result is in agreement with the electrode surfaces shown in Fig. 4, where it can be seen that corrosion spots decrease by increasing the CMS degree of substitution, while the metal surface remains bright when AS was employed. This evidences that starch molecules act as corrosion inhibitors of carbon steel and the protection level that they provide depends on the amount and type of active group present in the biopolymer: carboxylate (–COO$^-$) and alkoxy (–CO$^-$) groups for CMS, and alkoxy (–CO$^-$) groups for AS.

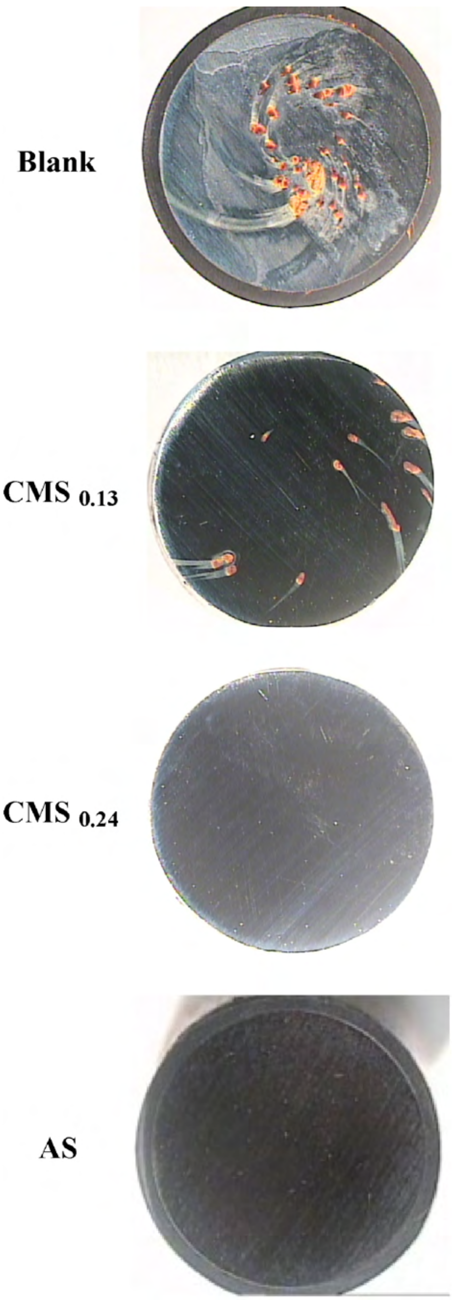

Fig. 4. Photographs of the XC 35 carbon steel surfaces after 2 h of immersion without inhibitor and in the presence of 600 mg L^{-1} of each inhibitor.

In previous works (Sancristobal, 2009), it was demonstrated by X-ray photoelectron spectroscopy (XPS), that the inhibitive film is composed by an iron oxide–hydroxide layer (Fe_2O_3 and $Fe(OH)_3$), in which starch molecules are incorporated. Thus, protection provided by these modified starches is related to the formation of an insoluble chelate between the active groups present in the inhibitor molecules and the ferrous cations generated when corrosion takes place. In agreement with other reports found in the literature (Ochoa et al., 2004; Suzuki, Nishihara, & Aramaki, 1996), this insoluble complex would seal the defects of a very thin layer of corrosion products, reducing metal dissolution.

Table 1
Electrochemical parameters obtained from the impedance diagrams presented in Fig. 3.

Solution	E_{corr} vs SCE (mV)	R_p (Ω cm^2)
Blank	−420 ± 7	1650 ± 307
CMS$_{0.13}$	−432 ± 10	11,600 ± 989
CMS$_{0.24}$	−425 ± 5	20,000 ± 1000
AS	−399 ± 15	57,450 ± 1023

Electrostatic potential mappings of AS and CMS monomeric units were carried out in order to explain the differences in the protection level achieved in the presence of each starch molecule and they are presented in Fig. 5. Calculations were carried out from the salt form units (Na-CMS and Na-AS) removing only one sodium cation from the carboxylate and alkoxy groups, respectively. Mapping on this isosurface the $V(r)$ values onto colors allows

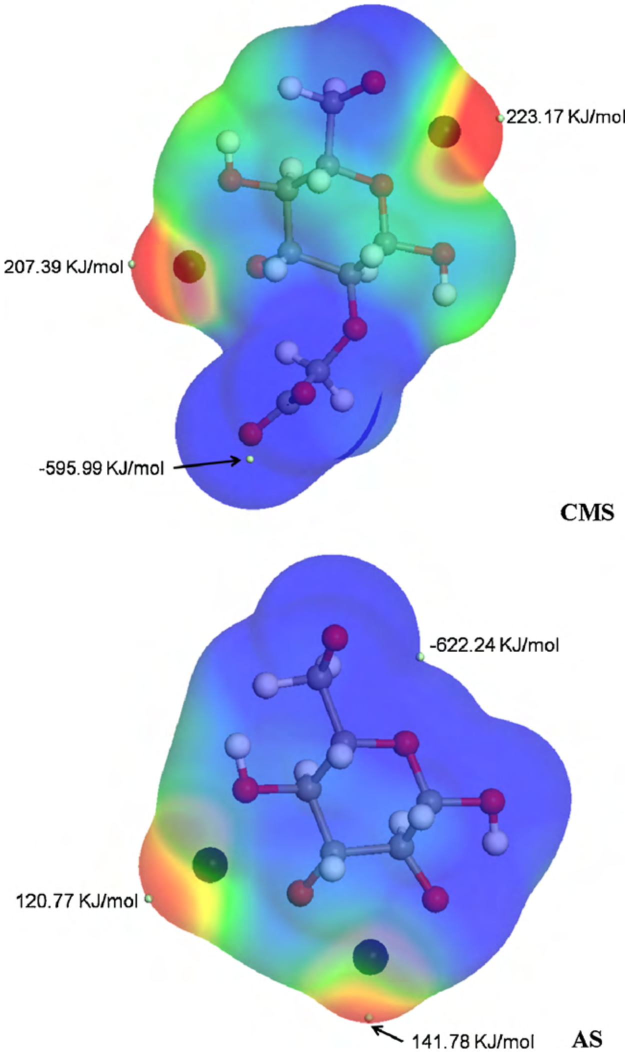

Fig. 5. Electrostatic potential mapping of the CMS and AS monomeric unit. White, red, gray and black spheres correspond to H, O, C, and Na atoms, respectively. Small light green spheres localize the maxima (at the acid zones) and the minima (at the basic zones). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

identifying the host sites in which nucleophiles (most positive zone) and electrophiles (most negative zone) should bind. As it is illustrated in the figure, positive and negative zones are represented in red and blue colors, respectively. Thus, blue zones are located around –COO$^-$ and –CO$^-$ species; these zones would interact with the metal surface forming an insoluble chelate according to the inhibition mechanism proposed above. As it may be seen, AS has a more negative electrostatic potential than CMS; this suggests that AS would strongly interact with the metallic surface. This result combined with the lower hydrophilicity (Heinze & Koschella, 2005) and higher molecular weight (Contó, 2008) of AS explain the higher polarization resistance values obtained in the presence of this compound. On the other hand, the lower protection level achieved in the presence of CMS$_{0.13}$ is related to its lower amount of active groups compared to those available in CMS$_{0.24}$ (Bello, Ochoa, Balsamo, & Sancristobal, 2010). Indeed, the degree of substitution indicates that the amount of carboxylate groups decreased in 50%.

Since electrochemical results reveal that the protection level achieved by AS is higher than for CMS, inhibitive properties of this molecule were monitored during 24 h of immersion by impedance measurements. As shown in Fig. 6, it may be noticed that the size of the impedance diagrams shows a significant increase between 2 and 6 h of immersion and then it remains constant. In addition, from 6 h, a capacitive loop appears in the high frequency domain, which may be attributed to the development of a thin film that covers the metal surface as a paint coating (Duval, Keddam, Sfaira, Srhiri, & Takenouiti, 2002; Gabrielli, 1984). This result reveals that the protective properties of AS enhance with the immersion time; in fact, the electrode photographs presented in Figs. 7 and 8 show that the metal surface remains bright and that there are not traces of rust after 6 and 24 h of immersion.

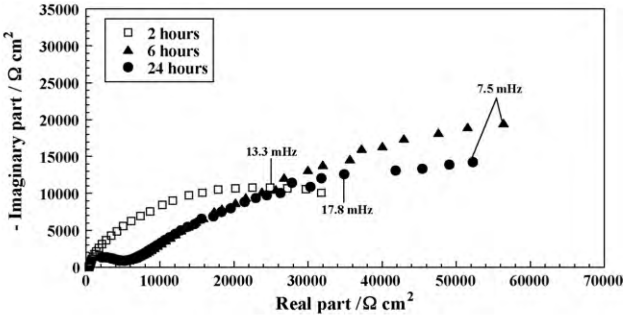

Fig. 6. Electrochemical impedance diagrams obtained after 2, 6 and 24 h of immersion at E_{corr} in the solution containing 600 mg L^{-1} of AS.

Inhibitive films formed in the presence of 600 mg L^{-1} of AS after 6 and 24 h immersion were analyzed by AFM in order to study the morphology of the corrosion protective layers. Figs. 7 and 8 show the images obtained from AFM of the inhibitive surfaces in AAC mode. Topography (2D and 3D), amplitude, and phase images are presented in order to get a better understanding of the AFM results. Independently of the immersion time, 3D topographic images reveal the presence of clusters on the metal surface; which correspond to the dark zones on the phase image. It is noteworthy that after 24 h of immersion, there is a higher concentration of clusters and they are distributed more homogeneously. This is especially evident in the phase image as the dark areas are much larger than those observed at 6 h of immersion, where smaller points of the same color are observed in a lighter matrix. In accordance with AFM fundamentals (Braga & Ricci, 2004; Yu & Magonov, 2007), phase imaging is very sensitive to surface properties such as stiffness, viscoelasticity, and chemical composition. Therefore, the color scale observed on the phase images indicates the presence of different kinds of materials on the metal surface, corresponding light and dark zones to harder and softer materials, respectively. Thus, according to the inhibition mechanism proposed for this type of compounds (Sancristobal, 2009), which was previously mentioned, light areas are attributed to the formation of a thin layer of corrosion products (iron oxides and hydroxides) and dark clusters are associated to the presence of activated starch molecules adsorbed on the surface. Furthermore, the small dark spots observed at 6 h of immersion in Fig. 7, are attributed to the insoluble complex formed between the alcoxy groups of AS and iron cations, which precipitates sealing pores and/or defects of the corrosion product layer. This corresponds to the first stage of the formation of a more homogenous and dense protective film. This in agreement with the characteristics signals of starch molecules and corrosion products obtained from XPS analysis in a previous work (Sancristobal, 2009). In addition, it should be mentioned that the clusters seem to follow a distribution pattern that may be related to the spatial conformation of the starch molecules, in which starch retrogradation may be playing a role (Thiré, Simao, & Andrade, 2003). Further studies are being carried out in order to have evidences of this phenomenon.

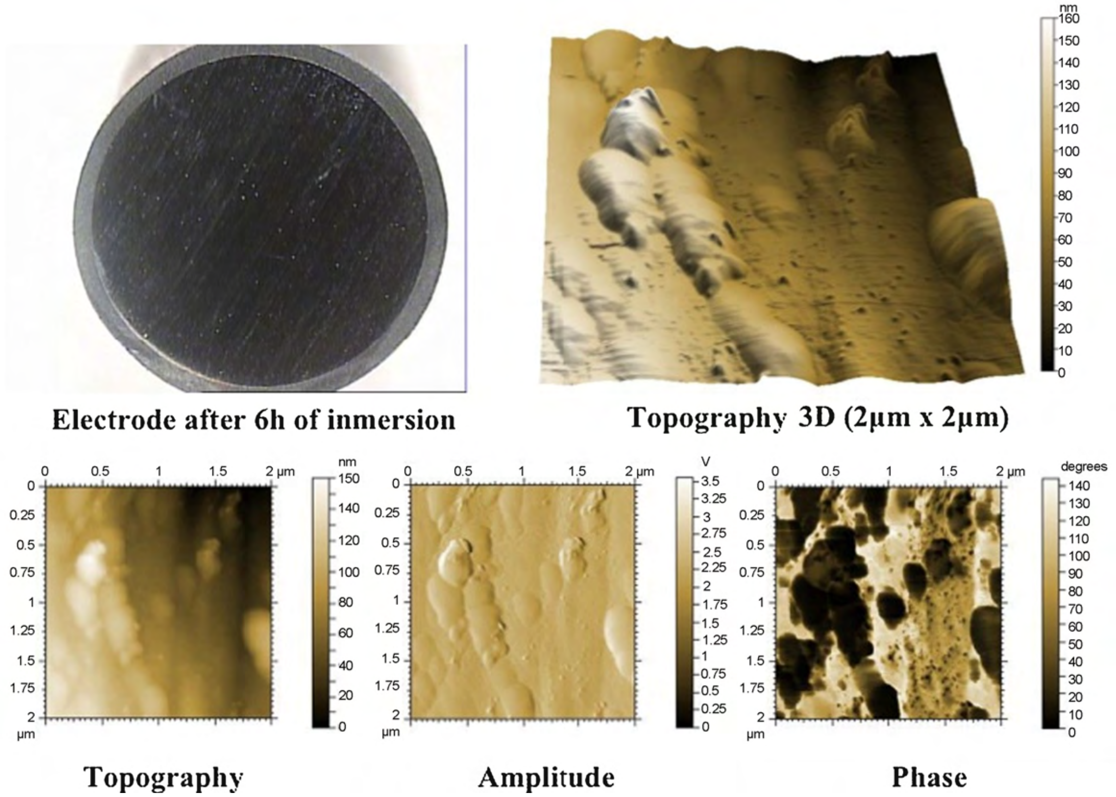

Fig. 7. AFM images of the XC 35 carbon steel surfaces after 6 h of immersion in the presence of 600 mg L^{-1} of AS.

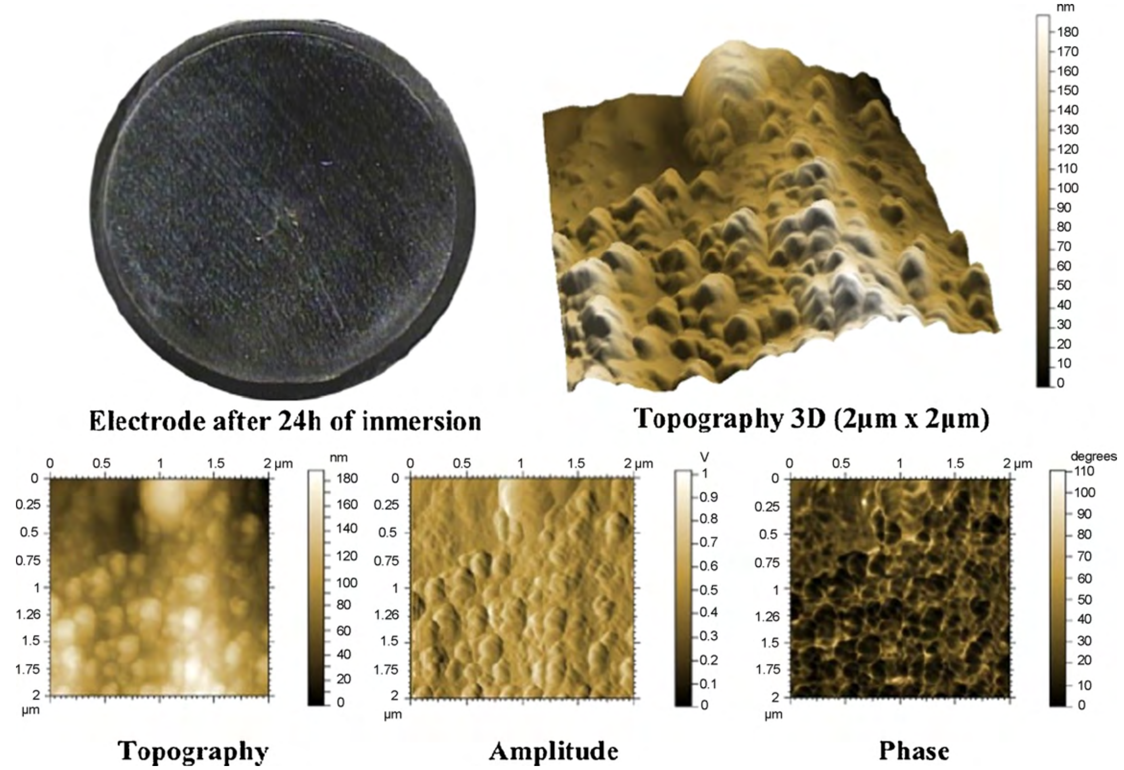

Fig. 8. AFM images of the XC 35 carbon steel surfaces after 24 h of immersion in the presence of 600 mg L^{-1} of AS.

4. Conclusions

From this study, it was demonstrated that activated and pregelatinized starches as well as carboxymethylated cassava starches behave as corrosion inhibitors of carbon steel in solutions that simulates tap water. The protection level that they provide depends on the amount and type of active groups present in the macromolecules. Even though it was found that the corrosion inhibitor performance of carboxymethylated starch (CMS) increases with the degree of substitution (*DS*), activated starch (AS) showed better inhibitive properties. This behavior was mainly attributed to the strong interaction of the active groups present in this molecule with the metallic surface and to its lower hydrophilicity; variations of molecular weight also were considered. Moreover, impedance measurements carried out in the presence of AS revealed that the polarization resistances values, which are inversely proportional to the corrosion rate, increase with immersion time. This fact, which was explained by the densification of the inhibitive film evidenced by AFM, is in agreement with the shiny surface of the electrode after 24 h of immersion. These results indicate that this biopolymer could be used as a potential commercial product for open cooling water systems, encouraging the employment of compounds based on the green philosophy.

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